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Accurate efficiency determination and stability studies of conjugated polymer/fullerene solar cells

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Abstract

We report on an accurate indoor determination of the power conversion efficiency under standard test conditions [1000 W/m², AM1.5 global (IEC 904-3), 25°C] for an organic photovoltaic device based on a bulk heterojunction of a conjugated polymer and a methanofullerene. AM1.5 efficiencies up to 2.55% are achieved for cell areas ≤ 1.0 cm². Systematic stability studies on encapsulated laboratory cells show that both thermal stress and visible light soaking leads to strong degradation of the cells. Degradation mechanisms have not yet been clearly identified. Morphological changes in the photoactive layer after thermal treatment as well as photochemical degradation of the polymers upon prolonged irradiation seem to have detrimental effects on the cell stability. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Solar cells; Conjugated polymers; Stability; Efficiency

1. Introduction

Accurate determination of the photovoltaic power conversion efficiency is essential for a comparison of results and product compatibility. Up to now, much experience has been built up in the characterisation of established inorganic solar cell technologies like crystalline silicon and gallium arsenide (GaAs). For these technologies, a high accuracy in the determination of power conversion efficiencies is not only of academic interest. It can also prevent developments in the wrong direction, because efficiency improvements resulting from one process step are usually in the range of 0.1% only. In order to quantify the cell performance in a comparable manner, a set of standard test conditions (STC) has been defined. These are specified as a radiant density of 1000 W/m² with a spectral distribution defined as ‘AM1.5G’ (IEC 904-3) at a cell temperature of 25°C.

For novel type of devices, like conjugated polymer-based solar cells as described in this paper, the deter-

mination of the power conversion efficiency is by far not settled. In spite of the STC, for organic solar cells in general all kinds of efficiencies have been reported, based on measurements performed under a large variety of conditions [1]. This makes a meaningful comparison of efficiency values, measured at different laboratories extremely difficult. It is, therefore, of general importance to pay more attention to accurate characterisation of these novel solar cells [2]. The present paper reports the results of accurate indoor measurements on conjugated polymer/fullerene solar cells performed under appropriate STC.

Substantial power conversion efficiencies of 2.5% at an illumination intensity of 80 mW/cm² and a cell temperature of 55°C have recently been reported for these potentially low cost ‘plastic’ photovoltaic cells based on interpenetrating networks of conjugated polymers and fullerene derivatives [3,4]. An efficiency value of 2.5% can be regarded as an encouraging breakthrough in realising higher efficiencies for polymer-based solar cells, but a common problem for all applications of conjugated polymers is stability. The utilisation of all organic devices needs at least operational lifetimes of several thousands of hours for commercial applications.

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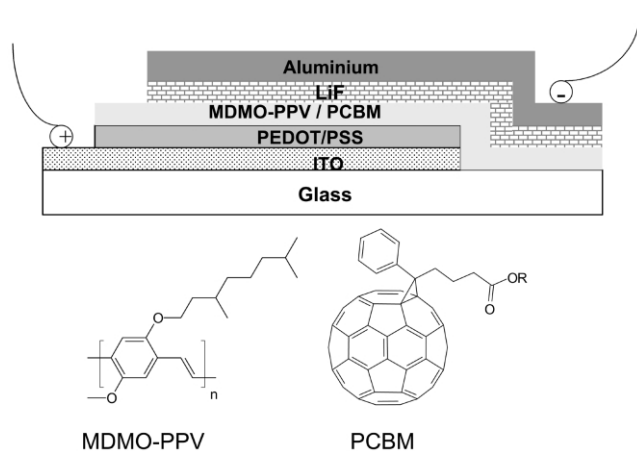


Fig. 1. Device structure of the solar cell and the chemical structures of MDMO-PPV and PCBM ($R = \text{Me}$).

Systematic stability studies are reported [5] on conjugated polymer/fullerene solar cells in an inert atmosphere and indicated accelerated degradation of the devices at higher temperatures and prolonged exposure to bright light. In addition to these investigations, we present preliminary stability studies on encapsulated devices.

2. Experimental

2.1. Device fabrication

The cells are prepared by procedures described in literature [2]. The cell configuration is shown in Fig. 1.

Poly [2-methoxy, 5-(3',7'-dimethyl-octyloxy)]-*p*-phenylene-vinylene (MDMO-PPV, from Covion) was used as the electron donor and [6,6]-Phenyl C₆₁-butyric acid methyl ester (PCBM, from J.C. Hummelen) as the electron acceptor.

Transparent pre-structured ITO/glass substrates (obtained from Philips Research) are used as front electrode. A PEDOT-PSS layer (Bayer AG, EL-Grade) of 100 nm is spincoated on top of the ITO layer from an aqueous suspension. The photo-active layer (~80 nm) is spincoated from a chlorobenzene solution with a 1:4 weight ratio of MDMO-PPV and PCBM. As top-electrode, a thin LiF (~1 nm) and subsequently a 100-nm Al layer are deposited on top of the organic layers by thermal evaporation. The device consists of four cells with different active areas: 0.1; 0.17; 0.33; and 1 cm², respectively.

To permit transportation the devices outside the nitrogen flushed glovebox encapsulation is mandatory. The sealing material used is Surlyn®/Al/PET foil, which is applied to the substrate with a hot stamp at 150°C. A secondary epoxy-glue is used for further protection. No loss of device performance is observed directly after the sealing step.

2.2. Measurement procedure for efficiency determination

For accurate indoor photovoltaic measurements under STC a solar simulator is employed, with a light spectrum that approximates the AM1.5 global spectrum and a calibrated reference cell to set the intensity. The measurement is divided into two steps: (a) the determination of the solar simulator spectral mismatch factor, M ; and (b) measurement of the I - V curve of the solar cell and correction to STC.

The match between the simulator spectrum, $E_s(\lambda)$ and the AM1.5G reference spectrum, $E_R(\lambda)$, is never perfect. Furthermore, a spectral mismatch is introduced since the spectral responses of the test device, $S_T(\lambda)$ and of the reference cell, $S_R(\lambda)$, are, in general, not identical. To correct for this, a spectral mismatch factor M is computed via the following formula:

$$M = \frac{\int E_R(\lambda) S_R(\lambda) d\lambda}{\int E_S(\lambda) S_R(\lambda) d\lambda} * \frac{\int E_S(\lambda) S_T(\lambda) d\lambda}{\int E_R(\lambda) S_T(\lambda) d\lambda} \quad (1)$$

where each integral in Eq. (1) is proportional to the short-circuit current that would be produced, at standard temperature, by the cell of stated spectral sensitivity $S_i(\lambda)$ under the specified spectrum $E_j(\lambda)$.

For crystalline silicon solar cells, M usually lies in the range 0.98–1.02, since stable calibrated reference cells are constructed from more-or-less the same material as the test cell. However, for the novel type of solar cells under the present study, suitable and stable reference cells cannot be fabricated yet. This implies that one has to use calibrated reference cells with a different spectral response as compared to the test device, resulting in mismatch factors significantly deviating from 1. Therefore, step (a) is the measurement of the spectral sensitivity functions of the reference cell and the test cell and measurement of the spectrum of the solar simulator. These measurements, together with the defined spectrum AM1.5G, enable M to be calculated. It is of utmost importance to carry out the procedure as precisely as possible in order to minimise the measurement errors.

For correct quantification of efficiencies, a standard procedure with certified equipment is prescribed. This includes determination of the spectral response of the solar cell according to the ASTM E1021-84 norm. This method is based on continuous irradiation of the test-device to maintain one sun working conditions. The spectral response is revealed using pulsed monochromatic illumination by means of a chopped light beam. A lock-in technique is used to distinguish the pulsed current output signal from the total output current. It is important to note that the response time of the test

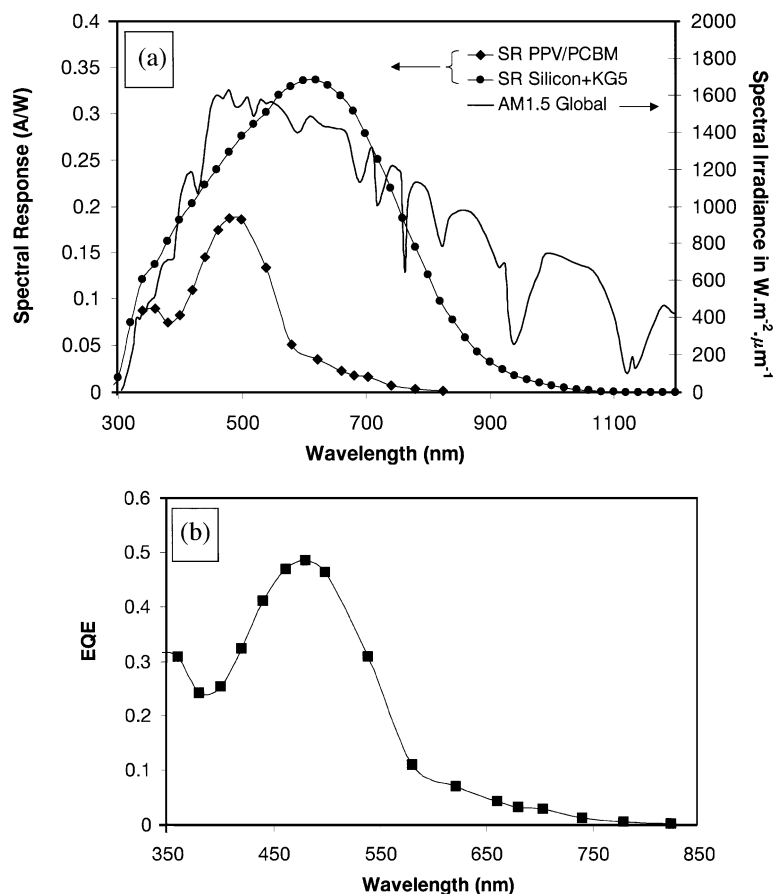


Fig. 2. (a) Spectral response (SR) in Ampere/Watt (A/W) of a 1.0-cm² ITO/PEDOT/(MDMO-PPV:PCBM)/LiF/Al device and a filtered (KG5) Silicon reference cell + the AM1.5 Global solar spectrum; and (b) the external quantum efficiency (EQE) of a 1.0-cm² ITO/PEDOT/(MDMO-PPV:PCBM)/LiF/Al device as calculated from the SR. The experiments are carried out as described in the experimental section

device under the standard measuring conditions (i.e. with bias light) should be much faster than the period of illumination by chopped light. This guarantees a constant output level, which is of crucial importance to analyse the signal correctly with the lock-in amplifier.

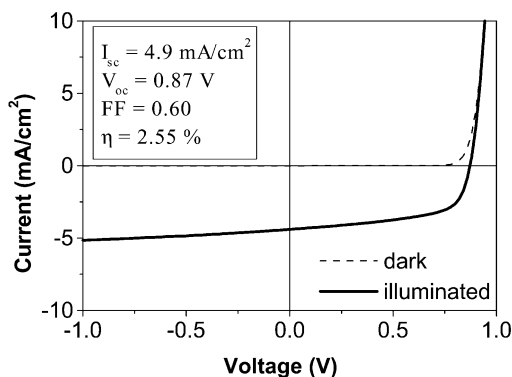


Fig. 3. The I - V characteristics of a 0.1-cm² ITO/PEDOT-PSS/(MDMO-PPV:PCBM)/LiF/Al device (dark + illuminated) at standard test conditions (AM1.5G, 1000 W/m², 25°C) after mismatch correction.

Since the response time of the conjugated polymer/fullerene solar cells was fast enough (<1 ms) to follow the least required chopper rate, successful spectral response measurement could be performed using a chopper frequency of 10 Hz.

At ECN, a Spectrolab XT-10 solar simulator is used. Solar cell efficiencies are measured according to the international standard norms (ASTM, IEC) [6]. For the conjugated polymer/fullerene solar cells, a monocrystalline Silicon solar cell + KG5 filter calibrated at Fraunhofer, Institut Solare Energiesysteme in Freiburg (Germany) is used as the reference cell. I - V curves are measured with a Keithley SMU 2400. The test cell is placed on a copper plate, which is temperature controlled and height adjustable. The exact temperature inside the polymer cell was measured using a dummy cell containing a thermocouple.

2.3. Stability testing

Continuous strong light soaking and on-line characterisation of the photovoltaic parameters is done in a home-build test facility consisting of a sulphur plasma

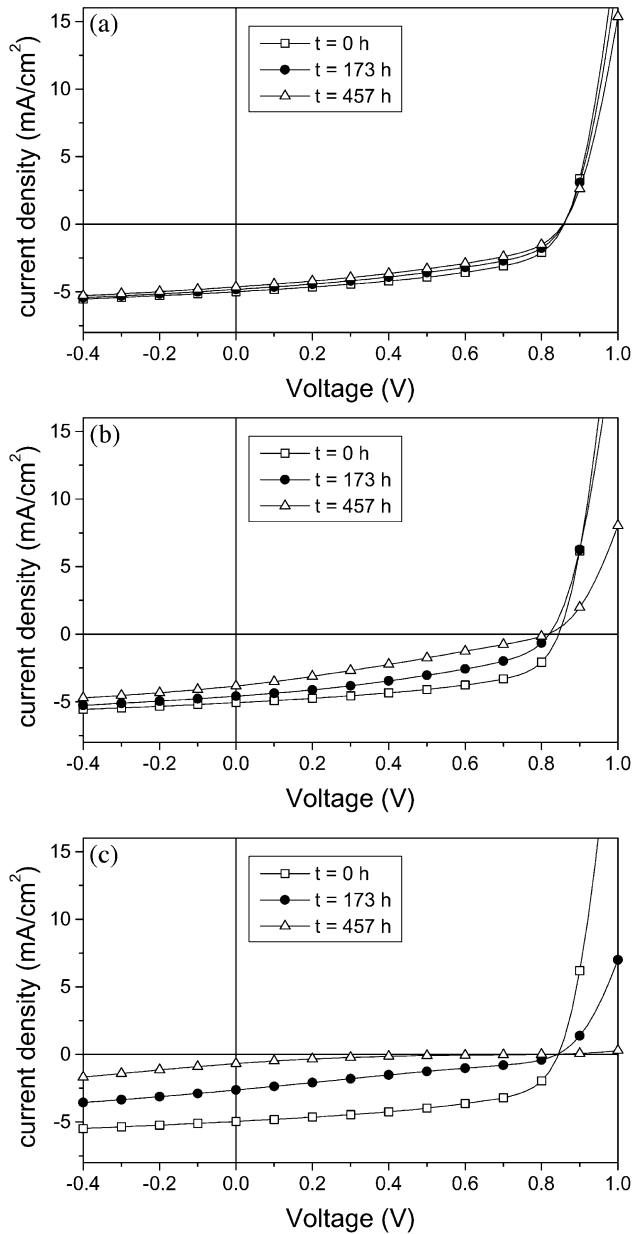


Fig. 4. Current–Voltage curves for 0.1-cm² cells measured at $t=0$, 173 and 457 h upon ageing at (a) room temperature, dark, (b) 40°C, dark and (c) 50°C, illumination

light source. The output of this lamp is continuous from 400 to 800 nm, with its maximum at 500 nm.

2.4. Light beam induced current measurements (LBIC)

A light beam (light source: Xenon lamp) with a spot diameter of 0.5 mm is transported over the area of a 1-cm² cell while the induced short-circuit currents from the locally illuminated areas are measured by means of a Keithley 2400 SMU.

3. Results and discussion

3.1. AM1.5 efficiency measurements

In step (a) of the measurement procedure, the spectral response of an encapsulated ITO/PEDOT/(MDMO-PPV:PCBM)/LiF/Al device is measured relative to the spectral response of the reference cell. The Spectral Response (SR) of the MDMO-PPV/PCBM device and the reference cell together with the AM1.5 Global spectrum are shown in Fig. 2a, while the external quantum efficiency (EQE) spectrum, or incident photon to current efficiency (IPCE), of the polymer device is shown in Fig. 2b. The latter shows a maximum EQE of 0.5 at approximately 480 nm, identical to the EQE values as reported by Shaheen et al. [3].

Together with the spectral distribution for AM1.5G and the simulator spectrum (not shown), a mismatch factor of 0.9 is calculated using Eq. (1). This value is used in step (b) to correct the measured I_{sc} values of the polymer-fullerene cell to I_{sc} values appropriate to AM1.5G conditions. This is done by adjusting the solar simulator up to the point where $I_{sc} = I_{sc,ref}/M$. After performing a current–voltage (I – V) measurement of the ITO/PEDOT/(MDMO-PPV:PCBM)/LiF/Al cell, the power conversion efficiency, η , is calculated according to Eqs. (2) and (3):

$$\eta = \frac{P_{out}}{P_{in}} = FF \frac{V_{OC} I_{SC}}{P_{in}} \quad (2)$$

where P_{out} is the maximum output electrical power of the device under illumination and P_{in} is the light intensity incident on the device, V_{oc} is the open-circuit voltage, I_{sc} is the short-circuit current. The fill factor, FF , is given by:

$$FF = \frac{V_{mpp} I_{mpp}}{V_{OC} I_{SC}} \quad (3)$$

where V_{mpp} and I_{mpp} are the voltage and current at the maximum power point, respectively.

A plot of the current density versus voltage is shown in Fig. 3 for a 0.1-cm² cell. An AM1.5 efficiency of 2.5% could be calculated from the I – V parameters, which is again similar to the reported value of Shaheen et al. [3,4]. Somewhat lower efficiency values (2.3%) were obtained for 1.0-cm² cells, which is caused by series resistance losses (lower fill factors) in the conducting oxide, mainly due to unfavourable geometrical design of the cell.

3.2. Stability studies

Preliminary studies have been done to investigate the stability of encapsulated ITO/PEDOT/(MDMO-PPV:PCBM)/LiF/Al devices. Three devices of each four cells were prepared and subsequently aged at open

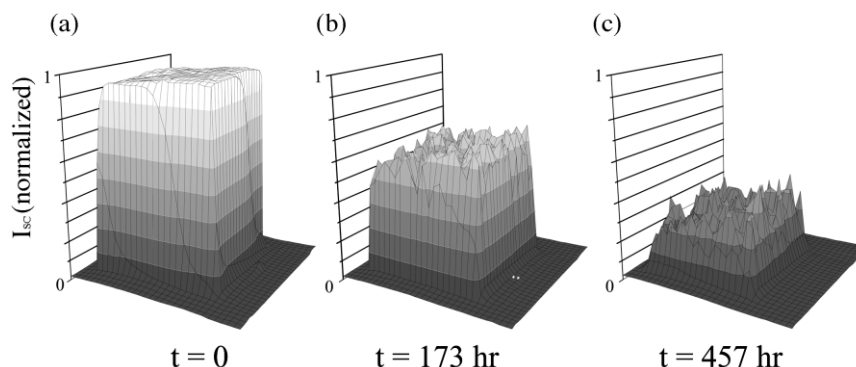


Fig. 5. The LBIC plots taken at (a) 0, (b) 173 and (c) 457 h after visible light soaking at 45°C for a 1-cm² cell.

circuit in the dark at room temperature, in the dark at elevated temperatures (at approx. 40°C) and by continuous illumination in the STF4 tester at 1 sun equivalent at 50°C. The results after 460 h of ageing are shown in Fig. 4. The cells, which are kept in the dark at room temperature remain stable in terms of I_{sc} and V_{oc} , while FF shows a slight decrease (10%), resulting in a small decrease of efficiency over time. At 40°C in the dark, a substantial decrease of I_{sc} and FF is observed, while V_{oc} remains constant, resulting in an overall decrease of

30–50% in the efficiency. The combination of thermal stress at 50°C and visible light soaking show almost complete degradation of the cell within 460 h of ageing.

We have used the local light beam induced current (LBIC) technique as an additional tool for characterising the degradation of the devices. LBIC-plots are shown in Fig. 5 for a 1.0-cm² cell after different periods of illumination at 50°C. In freshly prepared devices, a fairly homogeneous current distribution is found, indicating that the spin cast procedure leads to smooth, homogeneous films. As can be seen in Fig. 5, the decrease in current density is relatively constant over the cell area, i.e. no local degradation is observed. This was also observed for the cells aged under dark conditions (data not shown).

Reflection spectra of the devices before and after ageing in the dark at room temperature and 40°C reveal no thermal degradation of the photoactive materials (see Fig. 6a). After light soaking at 50°C, an increase in the reflectance is observed in the wavelength region between 450 and 550 nm. In this region, the MDMO-PPV absorbs most of the light, indicating some photochemical degradation of the conjugated polymer (see Fig. 6b).

Stability of the conjugated polymer/fullerene solar cells is thought to depend on several factors. It is reported that during operation of the devices complicated sets of (photo-)chemical and oxidative processes can take place in the donor-acceptor blends and at the interfaces of the organic materials and electrodes, both in the absence and presence of oxygen [7]. Furthermore, the morphology of the blend plays a crucial role in efficient charge generation and charge carrier transport. The morphology of the blend has to be thermally stable up to 80°C in order to prevent further phase separation into larger and/or isolated (island) domains, which normally results in significantly lower current densities and fill factors.

Encapsulated devices have been used in our experiments and the quality of the sealant is such that leakage of water and oxygen from the environment does not play a significant role during the test period (<500 h).

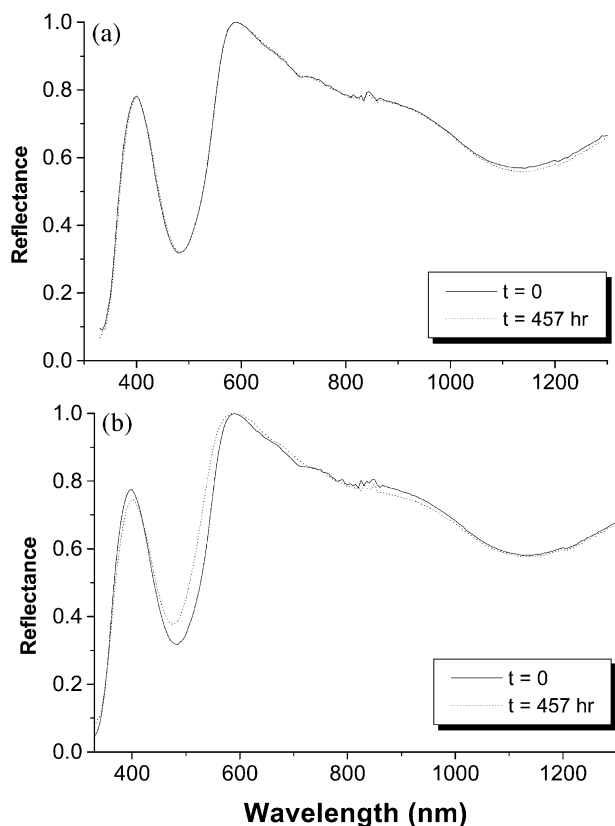


Fig. 6. The UV-VIS-NIR reflection spectra of cells measured before ($t=0$) and after ageing ($t=457$ h) at (a) 40°C, dark and (b) 50°C + illumination.

It is shown that degradation in the dark at room temperature is negligible, although a minor decrease in the FF is observed. By increasing temperature under dark conditions, a stronger decrease in I_{sc} and FF is found, but reflection spectra remain unchanged. This indicates that physical changes in the morphology, i.e. phase separation of the donor- and acceptor domains in the blend, lead to less efficient pathways for charge transport. A combination of thermal stress and continuous illumination of the devices with visible light accelerates the degradation of the devices. Besides morphological changes of the blend, the photochemical degradation of the conjugated polymers, as observed by the reflection spectra, has a detrimental effect on the performance of the solar cell.

The results described in this paper are only indicative. In order to better identify degradation mechanisms, more analytical techniques like TEM, Raman, FT-IR will be employed to gain insight into the influence of temperature on the morphology of the blends and the chemical factors responsible for degradation of polymer-based solar cells.

4. Concluding remarks

The standard method for determination of the spectral response according to ASTM E1021-84 is used for the conjugated polymer/fullerene solar cell. Following the complete procedure for accurate determination of the cell efficiency according to standard test conditions, an efficiency of 2.55% is achieved for a 0.1-cm² solar cell

based on the conjugated polymer MDMO-PPV and the methanofullerene derivative PCBM.

Stability tests show that accelerated degradation of the encapsulated devices occurs during visible light soaking and thermal ageing. The corresponding degradation mechanisms have not yet been clearly identified. Morphological changes in the photoactive layer after thermal ageing as well as photochemical degradation of the polymers after prolonged irradiation seem to have detrimental effects on the cell performance.

Acknowledgements

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References

- [1] J. Rostalski, D. Meissner, *Sol. Energy Mater. Sol. Cells* 21 (2000) 87.
- [2] E.A. Katz, D. Faiman, S.M. Tuladhar, J.M. Kroon, M.M. Wienk, T. Fromherz, F. Padinger, C.J. Brabec, N.S. Sariciftci, accepted *J. Appl. Phys.*
- [3] S.E. Shaheen, C.J. Brabec, N.S. Sariciftci, F. Padinger, T. Fromherz, J.C. Hummelen, *Appl. Phys. Lett.* 78 (2001) 841.
- [4] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Adv. Funct. Mater.* 11 (2001) 15.
- [5] F. Padinger, T. Fromherz, P. Denk, C.J. Brabec, J. Zettner, T. Hierl, N.S. Sariciftci, *Synth. Metals* 121 (2001) 1605.
- [6] P.M. Sommeling, H.C. Rieffe, J.A.M. van Roosmalen, A. Schönecker, J.M. Kroon, J.A. Wienke, A. Hinsch, *Sol. Energy Mater. Sol. Cells* 62 (2000) 399.
- [7] J.C. Hummelen, J. Knol, L. Sánchez, in: Z.H. Kafafi (Ed.), *Organic photovoltaics*, Proceedings of SPIE, 4108, 2001, p. 76.